

# The role of O- and S-containing surface groups on carbon nanotubes for the elimination of organic pollutants by catalytic wet air oxidation

Raquel P. Rocha, Adrián M.T. Silva, Saudi M.M. Romero,  
Manuel F.R. Pereira, José L. Figueiredo\*

*LCM – Laboratory of Catalysis and Materials – Associate Laboratory LSRE/LCM, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*

## ARTICLE INFO

### Article history:

Received 2 July 2013  
Received in revised form 30 August 2013  
Accepted 6 September 2013  
Available online 13 September 2013

### Keywords:

Catalytic wet air oxidation  
Carbon nanotubes  
Oxalic acid  
Phenol  
Surface chemistry

## ABSTRACT

Multi-walled carbon nanotubes (CNTs) were subjected to several liquid-phase chemical treatments (using  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , a mixture of  $\text{HNO}_3/\text{H}_2\text{SO}_4$ , HCl or bubbling  $\text{O}_3$  in water) as well as gas-phase thermal treatments under nitrogen atmosphere (at 200, 400 and 600 °C) in order to obtain CNTs with different chemical properties. The modified CNTs were characterized by common techniques including nitrogen adsorption at –196 °C, temperature programmed desorption, thermogravimetry, X-ray photoelectron spectroscopy and point of zero charge ( $\text{pH}_{\text{pzc}}$ ).

The  $\text{HNO}_3$  and  $\text{HNO}_3/\text{H}_2\text{SO}_4$  treatments induced a pronounced acidic character to the pristine CNTs (originally with a neutral  $\text{pH}_{\text{pzc}}$  of 6.8), creating a large amount of carboxylic acids, anhydrides and phenol surface groups, and also lactones and carbonyl/quinone surface groups. The treatment with  $\text{H}_2\text{SO}_4$  alone, or with the  $\text{HNO}_3/\text{H}_2\text{SO}_4$  mixture, led to the additional introduction of S-containing groups (such as sulphonic groups), while  $\text{O}_3$  and HCl treatments did not affect significantly the surface chemistry.

The pristine and modified CNTs were studied as catalysts in the catalytic wet air oxidation (CWAO) process by using oxalic acid and phenol as model pollutants (at 140 and 160 °C, respectively, and 40 bar of total pressure). At the selected operating conditions, these pollutants are quite stable in the absence of a catalyst. However, a marked degradation of both compounds was observed in the presence of CNTs. The O-containing surface groups in CNTs (carboxylic acids, phenols, anhydrides) contribute to the acidic character of the surface, and, simultaneously, decrease the catalytic activity for degradation of the tested pollutants. The presence of S-containing groups also increases the acidity of the CNTs, but a marked increase of the catalytic activity was observed in this particular case (complete degradation of the pollutants, 56% of TOC reduction in 120 min when phenol was the pollutant, and complete mineralization of oxalic acid). Therefore, the presence of S-containing groups and the absence of carboxylic groups (such as carboxylic acids and anhydrides) seem to improve the catalytic performance of CNTs; however, the S-containing materials are not stable in consecutive runs, probably as a result of the high temperatures and pressures employed in the CWAO process.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Carbon materials are clearly preferred catalysts for several environmental processes, including the liquid-phase oxidation of organic pollutants with different oxidizing agents (e.g., oxygen, ozone, hydrogen peroxide) [1]. For instance, carbon xerogels [2,3], activated carbons [3–11], carbon fibres and foams [12] and carbon nanotubes [13–15] were already studied as catalysts for the CWAO process. It is known that the catalytic performance of these carbon materials depends on their surface chemistry and textural properties, which can be tuned by adequate methods of synthesis

and/or by post-treatments [1,16,17]. In the particular case of carbon nanotubes, they have been already used as catalysts (without any metal phases) in several published works dealing with CWAO [7,13–15,18,19], due to their well-known mechanical and thermal properties [20] and also because the typical problems associated to supported metal catalysts can be avoided, such as leaching of the active phase which is a quite frequent deactivation phenomenon in oxidation reactions with transition metal catalysts [21–23].

Basic sites (or low acidic character) have been identified by some authors as the most favourable, not only for CWAO [13,19,22], but also for other advanced oxidation process (e.g., catalytic ozonation [24,25]). In contrast, other authors [14,15,18] have reported a positive effect of carboxylic acid surface groups when carbon nanotubes were used for the degradation of phenol by CWAO. Therefore, there is a controversy in the literature regarding the active sites of carbon

\* Corresponding author. Tel.: +351 225081663.

E-mail address: [jfig@fe.up.pt](mailto:jfig@fe.up.pt) (J.L. Figueiredo).

nanotubes (i.e. sites of basic or acidic nature) required to achieve the best performance in the CWAO process.

The main purpose of the present work is to clarify this issue, namely to identify the most suitable surface properties of carbon nanotubes when they are used as catalysts (without any impregnated metal) in the CWAO process. Commercial carbon nanotubes were modified by different chemical and thermal treatments, different surface groups being incorporated onto the pristine carbon nanotubes. The presence/absence of such groups contributes to the acidity or basicity of the carbon surface, which enables to study the influence of these groups in the CWAO process. Oxalic acid and phenol were selected as model pollutants, since oxalic acid is a refractory short chain carboxylic acid appearing as end-product in other advanced oxidation processes, while phenol is a more complex molecule extensively studied in the literature (usually used as probe species to evaluate the process efficiency) which is also an organic pollutant commonly found in industrial effluents.

## 2. Experimental

### 2.1. Materials

Commercial multi-walled carbon nanotubes (CNTs) purchased from NANOCYL™ (NC3100 series) were subjected to different chemical and thermal treatments in order to modify the original surface properties. According to the manufacturer, the pristine CNTs (CNT-O) have an average diameter of 9.5 nm, average length of 1.5  $\mu\text{m}$  and carbon purity higher than 95%, being one of the CNTs with higher purity that are available in the market, as referred in a recent work [26].

In the liquid-phase oxidation treatment with nitric acid, 4 g of the CNT-O sample was treated with nitric acid at a concentration of 7  $\text{mol L}^{-1}$  at boiling temperature during 3 h, resulting in sample CNT-N. In order to produce different samples with successively lower acid character, thermal treatments under  $\text{N}_2$  were then applied to CNT-N: 1 g of the CNT-N sample was heated to 200 °C at 10 °C  $\text{min}^{-1}$  under  $\text{N}_2$  flow (100  $\text{cm}^3 \text{min}^{-1}$ ) and kept at this temperature for 1 h (CNT-N200). The same procedure was repeated at higher temperatures, 400 and 600 °C, resulting in the samples labelled as CNT-N400 and CNT-N600, respectively.

A sulphuric acid treatment was also employed in order to introduce acidic functional groups of a different nature on the surface of the pristine CNTs (CNT-S). This treatment was performed in a round-bottom flask immersed in a paraffin bath at 50 °C during 4 h using 2 g of CNTs per 150 mL of  $\text{H}_2\text{SO}_4$  (98%). In addition, a sample labelled as CNT-NS was prepared by refluxing the pristine CNTs with a  $\text{HNO}_3/\text{H}_2\text{SO}_4$  mixture (1:3 v/v) at 50 °C during 4 h, as described elsewhere [14].

The CNT-O sample was also treated using ozone as oxidant (CNT-O3): 2 g of original CNT-O were added to 700 mL of distilled water in a semi-batch reactor, at room temperature, and 150  $\text{cm}^3 \text{min}^{-1}$  of ozone (50  $\text{g O}_3 \text{ min}^{-1}$ ) was continuously fed during 5 h. Ozone was produced from pure oxygen in a BMT 802X ozone generator and its concentration in the gas phase was monitored with a BMT 964 ozone analyser. An additional sample was prepared from pristine CNTs, where 2 g of CNT-O were suspended in a 37% hydrogen chloride solution and placed in an ultrasound bath during 20 min at room temperature (CNT-HCl).

After all the above mentioned liquid-phase treatments, each sample was washed several times with distilled water until neutral pH of the rinsing water was attained and finally dried overnight at 110 °C in an oven. These materials are listed in Table 1.

**Table 1**

Textural properties of the pristine and treated CNTs determined from  $\text{N}_2$  adsorption isotherms.

Sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{ g}^{-1}$ )	$V_p$ ( $\text{cm}^3 \text{ g}^{-1}$ )
CNT-O	326	0.67
CNT-N	400	1.02
CNT-N200	408	1.10
CNT-N400	408	1.06
CNT-N600	389	1.03
CNT-NS	394	0.89
CNT-S	293	0.71
CNT-O3	333	0.80
CNT-HCl	333	0.80

### 2.2. Catalyst characterization

Nitrogen adsorption isotherms determined at -196 °C in a Quantachrome NOVA 4200e multi-station apparatus were used to evaluate the textural properties of the CNT samples. Surface areas of the carbon samples were determined according to the Brunauer, Emmett and Teller method ( $S_{\text{BET}}$ ) and the total pore volume ( $V_p$ ) determined from the  $\text{N}_2$  uptake at  $p/p_0 = 0.95$ .

The surface chemistry of the samples was characterized by temperature programmed desorption (TPD) analysis in a fully automated AMI-300 Catalyst Characterization apparatus (Altamira Instruments) connected to a Dycor Dymaxion Mass Spectrometer. In a typical run, 0.100 g of the sample was placed in a U-shaped quartz tube located inside an electrical furnace and heated up to 1100 °C at 5 °C  $\text{min}^{-1}$  using a constant flow rate of helium equal to 25  $\text{cm}^3 \text{ min}^{-1}$ . The CO and  $\text{CO}_2$  released during the thermal analysis were monitored, and the calibration of the respective gases was carried out at the end of each analysis. SO and  $\text{SO}_2$  signals were also monitored for the samples treated with sulphuric acid (CNT-S and CNT-NS). A sulphanilamide standard was used in this case for  $\text{SO}_2$  mass signal calibration.

X-ray photoelectron spectroscopy (XPS) was performed in a VG Scientific ESCALAB 200A spectrometer using a non-monochromatized  $\text{Mg K}\alpha$  radiation (1253.6 eV), the binding energies being calibrated with respect to the C1s peak at 285.0 eV.

The  $\text{pH}_{\text{pzc}}$  of the materials was determined by using a drift method described elsewhere [25,27]. The characterization of the materials was completed by thermogravimetric analysis (TGA), using a STA 490 PC/4/H Luxx Netzsch thermal analyser by heating the samples at 10 °C  $\text{min}^{-1}$  under nitrogen flow (50  $\text{cm}^3 \text{ min}^{-1}$ ) up to 900 °C.

### 2.3. Experimental procedure

CWAO experiments with phenol and oxalic acid were performed in a 160 mL 316-SS high pressure batch reactor housing a glass liner (Parr Instruments, USA Mod. 4564). In the case of oxalic acid, 75 mL of a 1000  $\text{mg L}^{-1}$  aqueous solution and 0.2 g of the catalyst sample were placed into the reactor. The reactor was flushed with pure nitrogen till complete removal of oxygen, pressurized with 5 bar of nitrogen and then pre-heated up to the desired temperature (140 °C) under continuous stirring at 500 rpm in order to ensure proper mass transfer of oxygen in the liquid phase [2,3]. When the desired temperature was reached, pure air was injected to obtain a total pressure of 40 bar inside the reactor (corresponding to 7 bar of oxygen partial pressure); this was considered time zero for the reaction ( $t = 0$ ). The carbon material was recovered at the end of each run for further characterization, or for reutilization in cyclic experiments. The same procedure was repeated for CWAO experiments of phenol but using in this case a temperature of 160 °C and a phenol concentration of 75  $\text{mg L}^{-1}$  in water. The

temperatures were selected after preliminary experiments at different temperatures, and the initial concentrations of oxalic acid and phenol were selected by taking into account the concentration of oxygen that is dissolved in the liquid phase at the selected temperatures and pressures. Adsorption experiments were also performed in the autoclave under similar experimental conditions but replacing air by pure nitrogen (40 bar of total pressure). In addition, non-catalytic wet air oxidation (WAO) runs were carried out as blank experiments for both model pollutants.

#### 2.4. Analytical techniques

Samples periodically withdrawn from the reactor were analysed by high performance liquid chromatography (HPLC) with a Hitachi Elite LaChrom system equipped with a Diode Array Detector (L-2450). For determination of oxalic acid concentration, a Bio-Rad Aminex HPX-87H column (300 mm × 7.8 mm) with a sulphuric acid solution (4 mmol L<sup>-1</sup>) at a flow rate of 0.6 cm<sup>3</sup> min<sup>-1</sup> (as mobile phase) was used. The quantification of oxalic acid was performed at  $\lambda = 210$  nm, with a maximum relative standard deviation of 2%. In phenol oxidation experiments, the samples were analysed in a Purospher Star RP-18 endcapped column (250 mm × 4.6 mm, 5 µm particles) working at room temperature. The mobile phase was a mixture of water and methanol 40/60 (v/v) with a flow rate of 1 mL min<sup>-1</sup>. The total organic carbon (TOC) was also determined at the end of each experiment, using a Shimadzu TOC-5000A analyser.

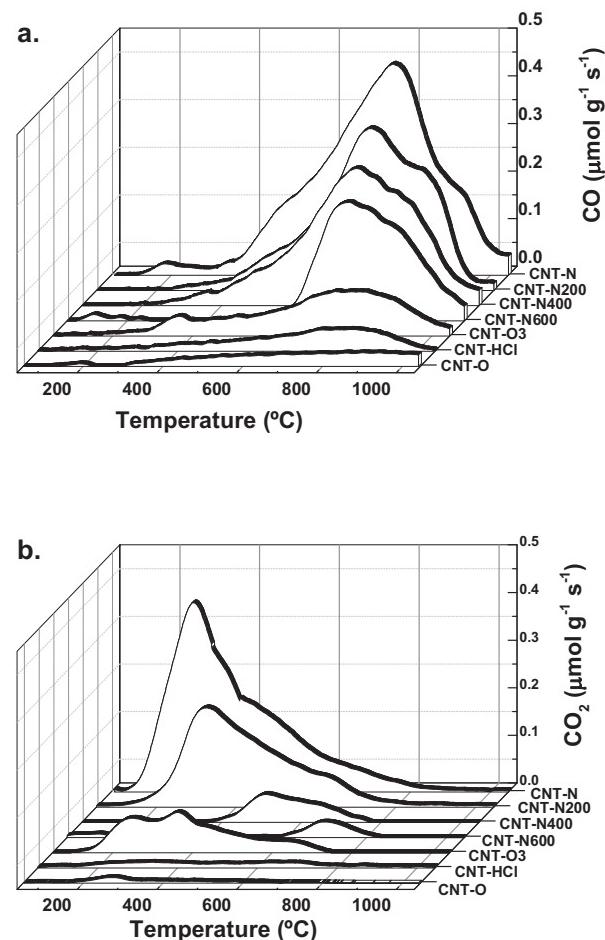
### 3. Results and discussion

#### 3.1. Characterization of pristine and treated CNTs

The chemical and thermal treatments applied to the pristine CNTs promote some modifications in their textural and surface properties. The N<sub>2</sub> adsorption isotherms of the original and modified CNT samples (not shown) can be classified as type II, according to IUPAC [28], which are characteristic of non-porous materials such as CNTs. In spite of the similar shape of the isotherms, it is possible to observe some specific differences in the amounts of N<sub>2</sub> adsorbed at high relative pressure (as shown by the total pore volume ( $V_p$ ) determined at  $p/p_0 = 0.95$ ) and in the  $S_{BET}$  values presented in Table 1. In all cases, linearity of the BET equation was observed in the range of relative pressures from 0.05 to  $\approx 0.3$ .

Oxidation with nitric acid (CNT-N) results in an increase of both  $S_{BET}$  and  $V_p$  (from 326 to 400 m<sup>2</sup> g<sup>-1</sup> for  $S_{BET}$  and from 0.67 to 1.02 cm<sup>3</sup> g<sup>-1</sup> for  $V_p$ , when CNT-O and CNT-N are compared, respectively). The thermal treatments applied to the CNT-N sample (samples CNT-N200, CNT-N400 and CNT-N600) did not promote significant additional changes on  $S_{BET}$  or  $V_p$ ; for instance, the differences between the surface areas of the treated samples were lower than 20 m<sup>2</sup> g<sup>-1</sup>, which is within the experimental error. The treatment with sulphuric acid (CNT-S) promotes slight changes in  $S_{BET}$  and  $V_p$  (to 293 m<sup>2</sup> g<sup>-1</sup> and 0.71 cm<sup>3</sup> g<sup>-1</sup>, respectively). The CNT-NS sample presents values of  $S_{BET}$  and  $V_p$  which are intermediate between those of CNT-O and CNT-N.  $S_{BET}$  was not affected by the treatments in the case of the CNT-O3 and CNT-HCl samples. The changes in  $V_p$  may reflect different degrees of agglomeration of the CNTs, as a result of different surface chemistries induced by functionalization. The BET surface areas of the nitric acid treated samples are about 400 m<sup>2</sup> g<sup>-1</sup>, and around 330 m<sup>2</sup> g<sup>-1</sup> for the others (including the pristine CNTs). This may indicate that the treatments with nitric acid might partially open some of the nanotube tips.

In order to identify and quantify the amount of oxygenated groups incorporated by the applied treatments, the surface chemistry of all samples was analysed by TPD. The CO and CO<sub>2</sub> spectra are shown in Fig. 1 (for CNT-O, CNT-N, CNT-O3 and CNT-HCl) and Fig. 2



**Fig. 1.** Spectra of (a) CO and (b) CO<sub>2</sub> evolved in TPD of pristine CNTs (CNT-O) and modified samples: nitric acid (CNT-N) and thermally treated (CNT-N200, CNT-N400, CNT-N600), ozone (CNT-O3) and HCl (CNT-HCl).

(for CNT-S and CNT-NS), indicating the release of anhydrides, phenols and carbonyl/quinone groups as CO (Figs. 1a and 2a) as well as carboxylic acids, anhydrides and lactones as CO<sub>2</sub> (Figs. 1b and 2b) [16,29,30].

It can be observed that oxidation with nitric acid (CNT-N) incorporates a large amount of oxygen containing groups on the CNTs (Fig. 1), as shown by the large increase in the amounts of CO and CO<sub>2</sub> released (Table 2), namely from 187 to 1852  $\mu\text{mol g}^{-1}$  for CO and from 33 to 1233  $\mu\text{mol g}^{-1}$  for CO<sub>2</sub>. In particular, the CO<sub>2</sub> spectrum (Fig. 1b) shows that CNT-N presents a large amount of carboxylic acid groups (released below 450 °C) and carboxylic anhydrides (evolved between 350 and 600 °C) while lactones (released above 600 °C) were found in lower amount. Regarding the CO spectrum (Fig. 1a), it is also possible to observe a remarkable formation of phenol (500–750 °C) and carbonyl/quinone groups (700–950 °C).

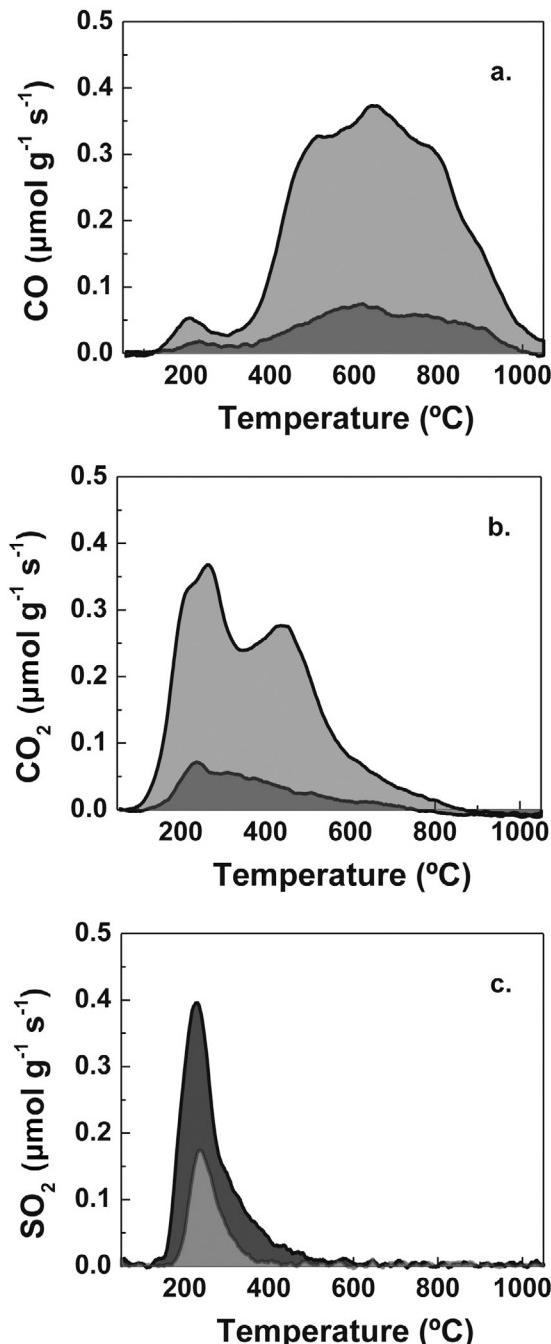
The thermal treatments applied to the CNT-N sample removed selectively those surface groups; thus, the CNT-N200 sample presents a lower amount of carboxylic acids than CNT-N. The remaining carboxylic acids were practically all removed as well as a part of the anhydrides when the treatment was performed at 400 °C (CNT-N400). After treatment at 600 °C (CNT-N600), the surface only contains phenol and carbonyl/quinone groups, and a small amount of lactones.

The liquid phase treatments with ozone (CNT-O3) and hydrogen chloride (CNT-HCl) did not affect significantly the surface chemistry of pristine CNTs (CNT-O), as revealed by the small amounts of CO and CO<sub>2</sub> evolved after these treatments.

**Table 2**

Surface chemistry characterization of the pristine and modified CNT samples.

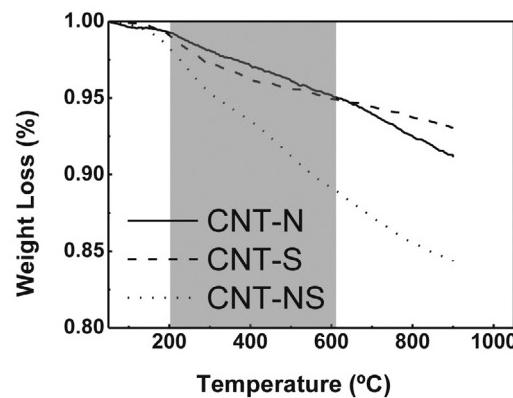
Sample	CO ( $\mu\text{mol g}^{-1}$ )	$\text{CO}_2$ ( $\mu\text{mol g}^{-1}$ )	$\text{SO}_2$ ( $\mu\text{mol g}^{-1}$ )	Volatiles <sup>a</sup> (wt.%)	pH <sub>pzc</sub>
CNT-O	187	33	–	1.8	6.8
CNT-N	1852	1233	–	9.5	2.2
CNT-N200	1308	727	–	8.0	2.5
CNT-N400	1205	113	–	5.2	4.8
CNT-N600	826	43	–	3.3	7.2
CNT-NS	2035	1397	203	16	4.8
CNT-S	381	195	579	7.3	2.5
CNT-O3	503	298	–	4.1	6.5
CNT-HCl	234	82	–	3.5	7.0

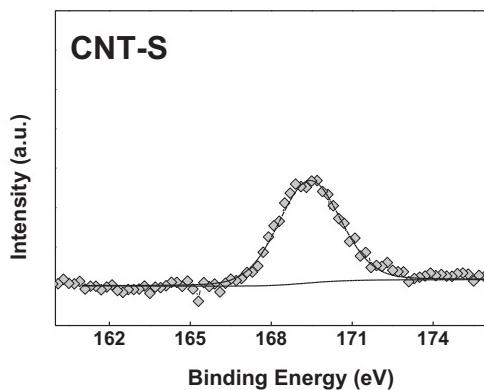
<sup>a</sup> Determined by TGA, in a dry ash free basis.**Fig. 2.** Spectra of (a) CO, (b)  $\text{CO}_2$  and (c)  $\text{SO}_2$  evolved in TPD of samples treated with sulphuric acid (CNT-S as dark grey) and with a mixture of sulphuric and nitric acid (CNT-NS as light grey).

On the other hand, as shown in Fig. 2a and b (light grey spectra), large amounts of various types of oxygen containing groups were successfully incorporated using the  $\text{H}_2\text{SO}_4/\text{HNO}_3$  mixture (CNT-NS), despite the low temperature employed in this treatment (50 °C). In contrast, as shown in the same figures (dark grey spectra), the amounts of CO and  $\text{CO}_2$  released during TPD were insignificant in the case of the sulphuric acid treatment (CNT-S), CO and  $\text{CO}_2$  increasing less than 200  $\mu\text{mol g}^{-1}$  when compared with the pristine sample.

For these two treated samples (CNT-NS and CNT-S), the MS signal of  $m/z = 64$  was also followed during the TPD analysis (Fig. 2c). The spectra reveal that desorption of S-containing groups occurs from the surface in a specific temperature range (200–400 °C), probably due to the decomposition of sulphonate groups into  $\text{SO}_2$  species [31]. In fact, the formation of these groups was already reported after a similar liquid-phase treatment performed over activated carbons [32,33]. In agreement with the  $\text{H}_2\text{SO}_4$  concentration used in each treatment, the CNT-S sample showed a richer surface than CNT-NS, with respect to S-containing groups, with nearly the triple amount of  $\text{SO}_2$  released (579 and 203  $\mu\text{mol g}^{-1}$  for CNT-S and CNT-NS, respectively).

An overall estimation of the amount of volatiles was also obtained by thermogravimetric analyses up to 900 °C under  $\text{N}_2$  atmosphere (Table 2). In agreement with TPD analysis, the amount of volatiles is higher (>7.0 wt.%) in the samples treated with nitric and sulphuric acids (i.e. CNT-N, CNT-S and CNT-NS), as well as in the CNT-N200 sample. In addition, the increase in the temperature of the thermal treatments of CNT-N originates a decrease of the total amount of volatiles (from 9.5 to 3.3 wt.%, for CNT-N and CNT-N600, respectively). Fig. 3 shows the results of thermogravimetric analysis under helium for CNT-N, CNT-NS and CNT-S. Here, it is possible to observe that the weight loss of CNT-S is higher than that observed for sample CNT-N between 200 and 400 °C, precisely in the range of temperature where  $\text{SO}_2$  is desorbed, while the weight loss of CNT-S became less pronounced than that of CNT-N

**Fig. 3.** Weight loss of CNT-N, CNT-S and CNT-NS samples determined by TGA.



**Fig. 4.** S2p XPS spectrum for the sulphuric acid treated carbon sample CNT-S.

above 600 °C, since above this temperature the surface groups from CNT-N that are not present in CNT-S are released (Figs. 1 and 2, respectively). The weight loss for CNT-NS is more notorious due to its significantly higher content of surface groups, including both O- and S-containing groups (Table 2).

The pH<sub>pzc</sub> of the samples was determined in order to study the nature of the carbon surface after each treatment (Table 2). CNT-N and CNT-S (besides CNT-N200) are the most acidic samples, with pH<sub>pzc</sub> values between 2.2 and 2.5. In agreement with all previous discussion, the thermal treatments performed over CNT-N decrease the acidic character of the sample (i.e. an increase of pH<sub>pzc</sub> with the temperature of treatment is observed, from 2.2 till 7.2, for CNT-N and CNT-N600, respectively), leading to a neutral surface when the highest temperature was employed (600 °C).

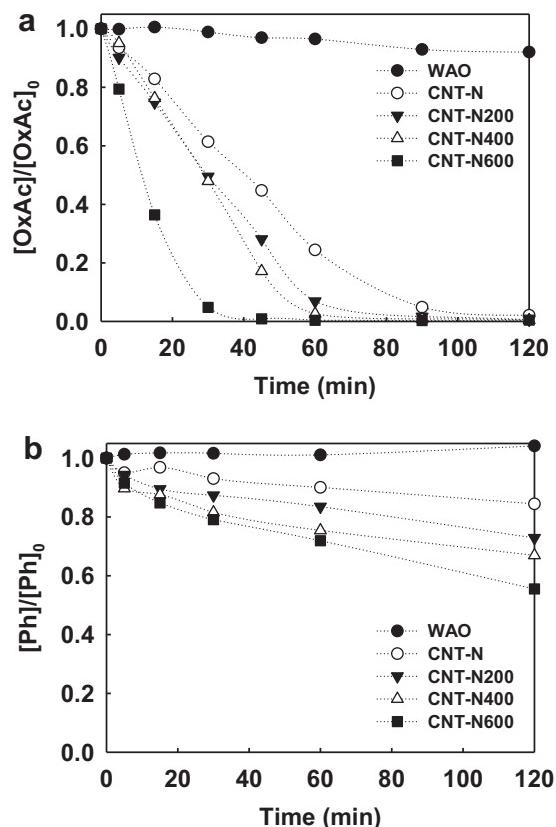
On the other hand, treatments with ozone (CNT-O3) or hydrogen chloride (CNT-HCl) do not promote any significant modification of the pH<sub>pzc</sub> of the pristine CNTs (CNT-O), the pH<sub>pzc</sub> remaining around 6.5 and 7.0, which is expectable because surface groups released as CO<sub>2</sub> are those with major effect on the acidity of carbon materials, and these treatments have little influence on the introduction of such groups onto the surface of CNTs (Fig. 1b).

The S2p spectrum of CNT-S (Fig. 4) shows a peak at 169 eV, which is the binding energy (BE) typically attributed to sulfonic groups ( $-SO_3H$ ) [34]. The absence of other peaks, especially at lower BE, allows concluding that other S-containing groups (such as thiol groups, 163 eV, and sulfides at 164 eV) are not incorporated during the treatment applied to the CNTs. Thus, we conclude that sulfonic acid groups were indeed incorporated on the surface of CNT-S.

### 3.2. Catalytic activity of CNTs

The catalytic activity of the pristine and modified CNTs was studied using oxalic acid and phenol as model pollutants. First, it is important to refer that the adsorption contribution was studied for all prepared materials and for both pollutants by performing experiments at the same conditions but replacing air by nitrogen. As expected, the adsorption of the model pollutants was negligible regardless the materials tested, due to the non-microporous nature of the CNTs.

In addition, Fig. 5a shows that oxalic acid is poorly oxidized in the absence of a catalyst (WAO) at 140 °C. In contrast, using CNTs treated with nitric acid (CNT-N) as catalyst, or even after subsequent thermal treatments (CNT-N200, CNT-N400 and CNT-N600), the degradation of oxalic acid is significantly increased, total degradation being achieved in less than 60 min with the CNT-N600 sample. The better catalytic performances obtained with the samples treated at higher temperatures can be related with the successive removal of the acidic groups (i.e. decrease in the amount of groups released as CO<sub>2</sub> and corresponding increase of pH<sub>pzc</sub>).

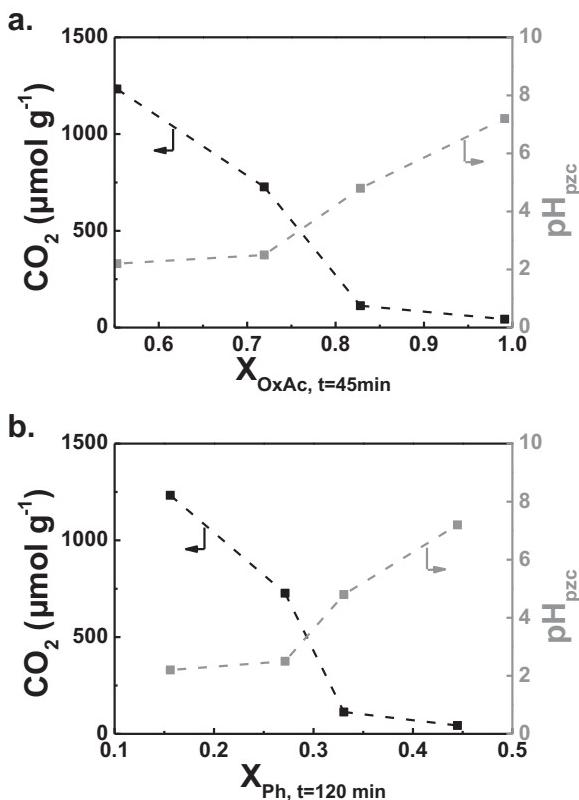


**Fig. 5.** Evolution of the normalized (a) oxalic acid and (b) phenol concentrations under non-catalytic conditions (WAO) and using the nitric acid and thermally treated samples as catalysts in CWAO.

The influence of the CNTs surface chemistry in the degradation of oxalic acid is clearly shown in Fig. 6a, where the amount of CO<sub>2</sub> released during the TPD analyses and the pH<sub>pzc</sub> of these samples were plotted against the oxalic acid conversions obtained in 45 min of reaction. Therefore, in general, the catalytic activity decreases as the acidity of the samples increases.

Phenol oxidation experiments were performed at 160 °C. Fig. 5b shows that phenol is not degraded in the absence of catalyst (WAO) and, once again, the sample treated at 600 °C (CNT-N600), which is also the less acidic sample of the set of materials shown in Fig. 5b, exhibits the best catalytic performance. The increase of the catalytic activity can be associated to the decrease of the acidic nature of these samples, as evidenced in Fig. 6b for this pollutant and as observed also for oxalic acid (Fig. 6a). Therefore, the conversion of phenol at 120 min of reaction increases with the decrease of the CO<sub>2</sub> amount released during the TPD experiments, as well as with the increase of the corresponding pH<sub>pzc</sub> of these samples.

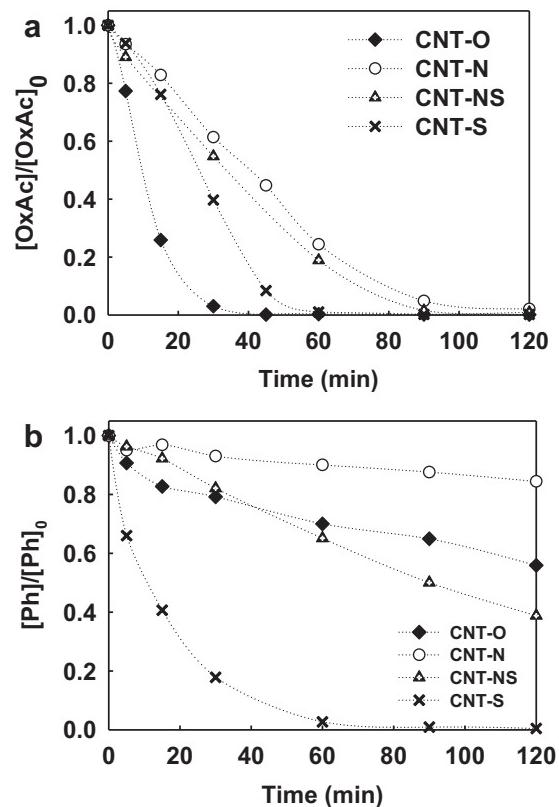
Therefore, the basic/acid nature of the CNTs seems to play an important role on the performance of these materials in CWAO experiments, as was already discussed in a previous work [13]. The results obtained in the present work are in agreement with the commonly reported effect of the basicity of carbon materials for liquid-phase oxidation reactions [12,16] and with other results observed in degradation of phenol by CWAO using activated carbon and/or CNTs, where the treatment with nitric acid has a negative effect on the catalytic activity of the carbon materials [7,19,22]. However, all these results seem to contradict other publications [14,15,18], where the carboxylic acid groups attached to the surface of CNTs have been claimed as promoting their catalytic activity for the oxidation of phenol by the CWAO process.



**Fig. 6.** Amount of  $\text{CO}_2$  released during the TPD analyses (left) and  $\text{pH}_{\text{pzc}}$  (right) of nitric acid and thermally treated samples, plotted against oxalic acid (a) and phenol (b) conversions obtained in 45 min and 120 min of reaction, respectively.

The catalytic performance of the pristine CNTs (CNT-O) and other prepared samples (CNT-S, CNT-NS and CNT-O3 and CNT-HCl) was also studied. Treatments with  $\text{O}_3$  or HCl have negligible effect on the catalytic activity; these two samples showed similar performance to the pristine CNTs, as expected, since these treatments also have little effect on the surface chemistry of the CNTs (Fig. 1). Fig. 7a and b shows the results obtained in the degradation of oxalic acid and phenol, respectively, when the other catalysts were employed. For comparative purposes, the results obtained with CNT-N are also included. Using the pristine CNTs (CNT-O), it is possible to achieve total conversion of oxalic acid in less than 60 min (Fig. 7a), as also observed for sample CNT-N600 (Fig. 5a), these two samples presenting the highest activity for oxalic acid degradation among all the set of tested materials. However, only 50% of phenol conversion is obtained by CWAO after 120 min of reaction when using the pristine CNT-O sample (Fig. 7b), the CNT-S and CNT-NS samples allowing higher conversions than CNT-O in 120 min of reaction.

Surprisingly, sample CNT-S, enriched with S-containing groups, shows the highest catalytic activity for the oxidation of phenol, 100% of phenol conversion being achieved after 90 min, in spite of the strong acidic character of this sample ( $\text{pH}_{\text{pzc}} = 2.5$ , Table 2). The CNT-S sample was also quite efficient for degradation of oxalic acid (Fig. 7a), in particular when compared with CNT-N and CNT-NS, 100% of oxalic conversion being achieved in 60 min. It is important to note that in the CWAO experiments with oxalic acid this pollutant was completely converted into  $\text{CO}_2$  (no by-products being detected by HPLC analysis, the TOC removal being equal to the oxalic acid disappearance), while only 57% of TOC conversion was achieved with sample CNT-S in the case of phenol, indicating that reaction by-products are formed and not totally degraded at the end of this experiment with phenol. In fact, several by-products are involved in the possible reaction pathways of phenol oxidation

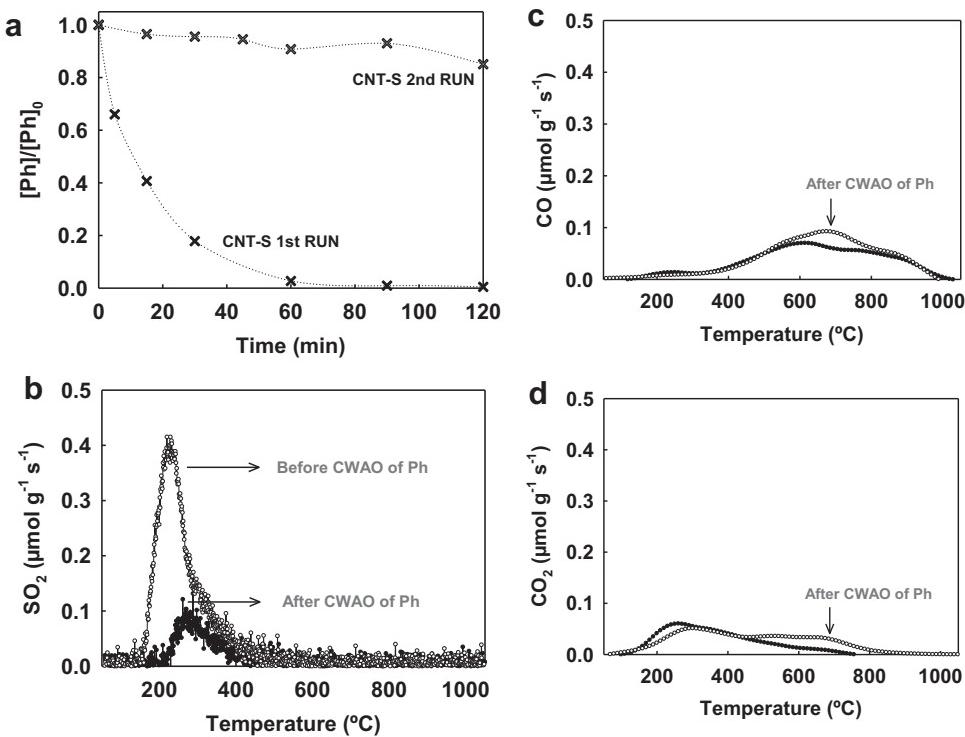


**Fig. 7.** Evolution of the normalized oxalic acid (a) and phenol (b) concentrations, using the nitric acid and sulphuric acid treated samples as catalysts in CWAO.

by CWAO [35], hydroquinone and benzoquinone being identified as the most representative intermediates, which were also detected in the present work together with oxalic acid.

In any case, the sample treated with the mixture of nitric and sulphuric acid (CNT-NS) showed better performance than CNT-N, and lower activity than CNT-S for both pollutants, but more notoriously with phenol (Fig. 7b). According to the TPD spectra, samples CNT-N (Fig. 1) and CNT-NS (Fig. 2) have large amounts of carboxylic acid groups, in contrast to CNT-S (Fig. 2), once again suggesting that the presence of carboxylic acids is not favourable for the reaction. In addition, all the carboxylic acid groups were removed after the thermal treatment of CNT-N at  $600^\circ\text{C}$  (i.e. CNT-N600), the TPD spectrum for CNT-600 regarding  $\text{CO}_2$  (Fig. 1b) being similar to that obtained for CNT-S (Fig. 2b), but a higher catalytic activity being observed for CNT-S. Therefore, the unexpected high catalytic performance of CNT-S has to be related to the S-containing groups that are incorporated in this sample (Fig. 2c). In fact, good catalytic activity of activated carbons containing sulphonate groups has already been reported for the catalytic wet peroxide oxidation of acid dyes [32,33].

In order to better understand the results obtained with CNT-S, its catalytic stability was investigated in cyclic experiments with phenol. Fig. 8a shows that this sample drastically loses its catalytic activity after the first run, only ca. 10% of phenol degradation being achieved in 120 min in the second run. The TPD spectra of this sample before and after the CWAO experiment with phenol are shown in Fig. 8b-d. It can be observed that most of the groups released as  $\text{SO}_2$  disappear after the CWAO run (Fig. 8b). The marked decrease of the catalytic performance of this sample after the first run (Fig. 8a) seems to be related with the disappearance of the S-containing groups. In fact, the high temperature and pressure used in the CWAO process could justify the removal of S-containing groups from the carbon surface, since the temperatures employed



**Fig. 8.** (a) Evolution of the normalized phenol concentration using the sulphuric acid treated sample as catalyst in cyclic CWAO runs, and spectra of (b)  $\text{SO}_2$ , (c)  $\text{CO}$  and (d)  $\text{CO}_2$  evolved in TPD of CNT-S catalyst before and after the first cycle.

(140–160 °C) are close to the temperature where  $\text{SO}_2$  desorbs (around 200 °C), and the high pressure could also play a role in the process. Therefore, the release of these groups to the liquid medium during the first experiment may lead to the formation of strong oxidant species, such as sulfate radicals, which are well known by their strong oxidizing potential [36]. The detection of lower amount of S-groups by TPD after the first run might be caused by fouling, as a result of deposition of phenol degradation products over the surface, blocking these groups. This possibility has been ruled out, because the TPD results show that only the evolved  $\text{SO}_2$  decreases after the 1st run (Fig. 8b), while the amounts of evolved  $\text{CO}$  and  $\text{CO}_2$  are similar, as shown in Fig. 8c and d.

The presence of S-containing groups can also justify the higher conversion obtained with CNT-NS after 120 min in comparison to CNT-N (Fig. 7b), both samples presenting quite similar TPD spectra with respect to  $\text{CO}$  and  $\text{CO}_2$  (Figs. 1 and 2 for CNT-N and CNT-NS, respectively), but CNT-NS having also a certain amount of groups released as  $\text{SO}_2$  (Fig. 2c) due to the use of  $\text{H}_2\text{SO}_4$  in its treatment. The CNT-NS sample is also slightly more active than CNT-N for the degradation of oxalic acid (Fig. 7a). Such observations could explain some results reported in literature, where CNTs subjected to oxidative treatments with mixtures of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  are employed for degradation of phenol by CWAO [14,15,18], at temperature and pressure conditions similar to those employed in the present work. Besides O-containing groups, such as carboxylic acids, S-containing groups can be also incorporated onto the CNTs after treatments with mixtures of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , these S-containing groups being responsible for the catalytic activity of the CNTs, instead of the carboxylic acid groups.

#### 4. Conclusions

Chemical and thermal treatments tested in this work showed a diversity of routes to modify commercial CNTs. Chemical treatments with  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and with a mixture of  $\text{HNO}_3/\text{H}_2\text{SO}_4$

incorporate different O-containing groups (carboxylic acids, anhydrides, phenols, carbonyl/quinones, lactones) onto the surface of CNTs or, when  $\text{H}_2\text{SO}_4$  is employed, S-containing groups (such as sulphonic groups). All these chemical treatments increase the acidic character of the CNTs, while thermal treatments remove the surface groups, simultaneously increasing the  $\text{pH}_{\text{pzc}}$  of the CNTs surface. Treatments with  $\text{O}_3$  or  $\text{HCl}$  do not affect significantly the CNTs surface chemistry.

Using the CNT samples treated with  $\text{HNO}_3$  and subjected to thermal treatments as catalysts for degradation of oxalic acid and phenol by CWAO, it was observed that the conversion of these pollutants increases as the  $\text{pH}_{\text{pzc}}$  of the materials increases, i.e., as the amount of O-containing surface groups present on the catalyst surface and released as  $\text{CO}_2$  decreases. However, CNTs modified with  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3/\text{H}_2\text{SO}_4$ , which have a strong acidic character (low  $\text{pH}_{\text{pzc}}$ ), showed an unexpected high activity for degradation of both model pollutants. The performance of these materials was explained by the presence of S-containing surface groups. In addition, the catalytic activity of the CNTs treated with  $\text{H}_2\text{SO}_4$  is drastically reduced in cyclic experiments due to the decomposition of the S-containing surface groups, as the result of the very high temperatures and pressures used in CWAO process.

Therefore, in general, the catalytic activity of CNTs increases with their basicity, but some specific groups, such as S-containing groups, can lead to a different behaviour even if they are acidic. In order to use CNTs as catalysts without any added metal, further studies are needed in order to obtain materials with higher stability.

#### Acknowledgments

This work was supported by project FREECATS financed by the European Union 7th FP (2007–2013), grant no. 280658 and by PEst-C/EQB/LA0020/2011, financed by FEDER through COMPETE – Programa Operacional Factores de Competitividade and by FCT – Fundação para a Ciência e a Tecnologia. S.M.M.R. acknowledges

the research fellowship PT/2012/17 under the IAESTE programme, while JL F acknowledges FCT grant SFRH/BSAB/1324/2012 and a sabbatical leave from Faculdade de Engenharia, Universidade do Porto.

## References

- [1] P. Serp, J.L. Figueiredo, *Carbon Materials for Catalysis*, John Wiley & Sons, Hoboken, NJ, 2009.
- [2] Â.C. Apolinário, A.M.T. Silva, B.F. Machado, H.T. Gomes, P.P. Araújo, J.L. Figueiredo, J.L. Faria, *Applied Catalysis B: Environmental* 84 (2008) 75–86.
- [3] H.T. Gomes, B.F. Machado, A. Ribeiro, I. Moreira, M. Rosário, A.M.T. Silva, J.L. Figueiredo, J.L. Faria, *Journal of Hazardous Materials* 159 (2008) 420–426.
- [4] C. Aguilar, R. García, G. Soto-Garrido, R. Arriagada, *Applied Catalysis B: Environmental* 46 (2003) 229–237.
- [5] T. Cordero, J. Rodríguez-Mirasol, J. Bedia, S. Gomis, P. Yustos, F. García-Ochoa, A. Santos, *Applied Catalysis B: Environmental* 81 (2008) 122–131.
- [6] S. Morales-Torres, A.M.T. Silva, A.F. Pérez-Cadenas, J.L. Faria, F.J. Maldonado-Hódar, J.L. Figueiredo, F. Carrasco-Marín, *Applied Catalysis B: Environmental* 100 (2010) 310–317.
- [7] M. Santiago, F. Stüber, A. Fortuny, A. Fabregat, J. Font, *Carbon* 43 (2005) 2134–2145.
- [8] M.E. Suárez-Ojeda, F. Stüber, A. Fortuny, A. Fabregat, J. Carrera, J. Font, *Applied Catalysis B: Environmental* 58 (2005) 105–114.
- [9] A. Katsoni, H.T. Gomes, L.M. Pastrana-Martínez, J.L. Faria, J.L. Figueiredo, D. Mantzavinos, A.M.T. Silva, *Chemical Engineering Journal* 172 (2011) 634–640.
- [10] V. Tukač, J. Hanika, *Collection of Czechoslovak Chemical Communications* 61 (1996) 1010–1017.
- [11] A. Fortuny, J. Font, A. Fabregat, *Applied Catalysis B: Environmental* 19 (1998) 165–173.
- [12] J.P.S. Sousa, A.M.T. Silva, M.F.R. Pereira, J.L. Figueiredo, *Separation Science and Technology* 45 (2010) 1546–1554.
- [13] R.P. Rocha, J.P.S. Sousa, A.M.T. Silva, M.F.R. Pereira, J.L. Figueiredo, *Applied Catalysis B: Environmental* 104 (2011) 330–336.
- [14] S. Yang, X. Li, W. Zhu, J. Wang, C. Descorme, *Carbon* 46 (2008) 445–452.
- [15] S. Yang, W. Zhu, X. Li, J. Wang, Y. Zhou, *Catalysis Communications* 8 (2007) 2059–2063.
- [16] J.L. Figueiredo, M.F.R. Pereira, *Catalysis Today* 150 (2010) 2–7.
- [17] J.L. Figueiredo, *Journal of Materials Chemistry A* 1 (2013) 9351–9364.
- [18] S. Yang, X. Wang, H. Yang, Y. Sun, Y. Liu, *Journal of Hazardous Materials* 233–234 (2012) 18–24.
- [19] M. Soria-Sánchez, A. Maroto-Valiente, J. Álvarez-Rodríguez, V. Muñoz-Andrés, I. Rodríguez-Ramos, A. Guerrero-Ruiz, *Applied Catalysis B: Environmental* 104 (2011) 101–109.
- [20] G. Ovejero, J.L. Sotelo, M.D. Romero, A. Rodríguez, M.A. Ocaña, G. Rodríguez, J. García, *Industrial & Engineering Chemistry Research* 45 (2006) 2206–2212.
- [21] J. Levec, A. Pintar, *Catalysis Today* 124 (2007) 172–184.
- [22] F. Stüber, J. Font, A. Fortuny, C. Bengoa, A. Eftaxias, A. Fabregat, *Topics in Catalysis* 33 (2005) 3–50.
- [23] A. Cybulski, *Industrial & Engineering Chemistry Research* 46 (2007) 4007–4033.
- [24] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, *Applied Catalysis B: Environmental* 79 (2008) 237–243.
- [25] A.G. Gonçalves, J.L. Figueiredo, J.J.M. Órfão, M.F.R. Pereira, *Carbon* 48 (2010) 4369–4381.
- [26] J.-P. Tessonnier, D. Rosenthal, T.W. Hansen, C. Hess, M.E. Schuster, R. Blume, F. Girgsdies, N. Pfänder, O. Timpe, D.S. Su, R. Schlögl, *Carbon* 47 (2009) 1779–1798.
- [27] J. Rivera-Utrilla, I. Bautista-Toledo, M. Ferro-García, C. Moreno-Castilla, *Journal of Chemical Technology & Biotechnology* 76 (2001) 1209–1215.
- [28] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, *Pure and Applied Chemistry* 57 (1985) 603–619.
- [29] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Órfão, *Carbon* 37 (1999) 1379–1389.
- [30] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Órfão, *Industrial and Engineering Chemistry Research* 46 (2007) 4110–4115.
- [31] A.P. Terzyk, *Journal of Colloid and Interface Science* 268 (2003) 301–329.
- [32] H.T. Gomes, S.M. Miranda, M.J. Sampaio, A.M.T. Silva, J.L. Faria, *Catalysis Today* 151 (2010) 153–158.
- [33] H.T. Gomes, S.M. Miranda, M.J. Sampaio, J.L. Figueiredo, A.M.T. Silva, J.L. Faria, *Applied Catalysis B: Environmental* 106 (2011) 390–397.
- [34] A.P. Terzyk, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 177 (2001) 23–45.
- [35] E.M. Sulman, V.G. Matveeva, V.Y. Doluda, A.I. Sidorov, N.V. Lakina, A.V. Bykov, M.G. Sulman, P.M. Valetsky, L.M. Kustov, O.P. Tkachenko, B.D. Stein, L.M. Bronstein, *Applied Catalysis B: Environmental* 94 (2010) 200–210.
- [36] C. Liang, H.-W. Su, *Industrial & Engineering Chemistry Research* 48 (2009) 5558–5562.